

518 Rec'd PCT/PTO D 2 AUG 2001

FORM PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER Mo-6479/LeA 33.510	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/890737 To be Assigned	
INTERNATIONAL APPLICATION NO. PCT/EP00/00576		INTERNATIONAL FILING DATE 26 January 2000 (26.01.00)		PRIORITY DATE CLAIMED 05 February 1999 (5.02.99)	
TITLE OF INVENTION METHOD FOR HYDROGENATING AROMATIC POLYMERS IN THE PRESENCE OF SPECIAL CATALYSTS					
APPLICANT(S) FOR DO/EO/US 1) Volker Wege; 2) Konstadinos Douzinas; 3) Johann Rechner					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).					
Items 11 to 20 below concern document(s) or information included:					
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input checked="" type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information:					
PTO Form 1449 and references listed therein; Preliminary Amendment w/Abstract					

U.S. APPLICATION NO. (if known) **02/890737**
To be assigned

INTERNATIONAL APPLICATION NO.
PCT/EP00/00576

ATTORNEY'S DOCKET NUMBER
Mo-6479/LeA 33,510

21. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO **\$1000.00**

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO **\$860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$690.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ **860.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	9 -20 =	0	x \$18.00	\$ 0.00
Independent claims	2 -3 =	0	x \$80.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00

TOTAL OF ABOVE CALCULATIONS =

\$ **860.00**

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.

\$ **0.00**

SUBTOTAL =

\$ **860.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE =

\$ **860.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

\$ **0.00**

TOTAL FEES ENCLOSED =

\$ **860.00**

Amount to be
refunded: \$
charged: \$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 860.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:



00157

PATENT TRADEMARK OFFICE

SIGNATURE

Aron Preis

NAME

29,426

REGISTRATION NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES RECEIVING OFFICE

518 Recd PCT/PTO 02 AUG 2001

Date	2 August 2001
International Application No.	PCT/EP00/00576
Attorney Docket No.	Mo-6479/LeA 33,510


09/890737

I. Certification under 37 CFR 1.10 (if applicable)

ET146886068US
Express Mail mailing number

2 August 2001
Date of Deposit

I hereby certify that the application/correspondence attached hereto is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Assistant Commissioner for Patents, Washington, D.C. 20231.


Signature of person mailing correspondence

Donna J. Veatch
Typed or printed name of person mailing correspondence

II. ☒ New International Application

TITLE	METHOD FOR HYDROGENATING AROMATIC POLYMERS IN THE PRESENCE OF SPECIAL CATALYSTS	Earliest priority date (Day/Mon/Year)
		(05/02/1999)

SCREENING DISCLOSURE INFORMATION: In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied. (Note: check as many boxes as apply):

- A. ☒ The invention disclosed was not made in the United States.
- B. ☒ There is no prior U.S. application relating to this invention.
- C. ☐ The following prior U.S. application(s) contain subject matter which is related to the invention disclosed in the attached international application. (NOTE: priority to these applications may or may not be claimed on form PCT/RO/101 (Request) and this listing does not constitute a claim for priority.)

application no.		filed on	
application no.		filed on	

- D. ☐ The present international application ☐ contains additional subject matter not found in the prior U.S. application(s) identified in paragraph C. above. The additional subject matter is found on pages and ☐ DOES NOT ALTER ☐ MIGHT BE CONSIDERED TO ALTER the general nature of the invention in a manner which would require the U.S. application to have been made available for inspection by the appropriate defense agencies under 35 U.S.C. 181 and 37 CFR 5.1. See 37 CFR 5.15

III. ☐ A Response to an Invitation from the RO/US. The following document(s) is(are) enclosed:

- A. ☐ A Request for An Extension of Time to File a Response
- B. ☐ A Power of Attorney (General or Regular)
- C. ☐ Replacement pages:

pages		of the request (PCT/RO/101)	pages		of the figures
pages		of the description	pages		of the abstract
pages		of the claims			

- D. ☐ Submission of Priority Documents

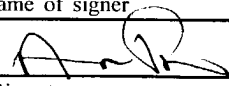
Priority document		Priority document	
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- E. ☐ Fees as specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☐ A Request for Rectification under PCT 91 ☐ A Petition ☐ A Sequence Listing Diskette

- V. ☒ Other (please specify): PTO Form 1449 and references listed therein; Preliminary Amendment w/Abstract

The person
signing this
form is the:

<input type="checkbox"/> Applicant	Aron Preis
<input checked="" type="checkbox"/> Attorney/Agent (Reg. No.) 29,426	Typed name of signer
<input type="checkbox"/> Common Representative	 Signature

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JC17 Rec'd PCT/PTO 02 AUG 2001
09/890737

PATENT APPLICATION
Mo-6479
LeA 33,510

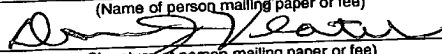
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
VOLKER WEGE ET AL) PCT/EP 99/00576
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: METHOD FOR HYDROGENATING)
AROMATIC POLYMERS IN THE)
PRESENCE OF SPECIAL CATALYSTS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231
Sir:

Prior to its examination kindly amend the English language translation of the enclosed application as follows:

"Express Mail" mailing label number ET146886068US
Date of Deposit August 2, 2001
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231
Donna J. Veatch
(Name of person mailing paper or fee)

Signature of person mailing paper or fee

Delete the Title of the application - appearing in pages 1 and 13 - and insert therefor:

-- Method for Hydrogenating Aromatic Polymers in the Presence of Special Catalysts --.

IN THE ABSTRACT:

Please revise the Abstract of the disclosure at page 13 to read:

"A process for hydrogenating aromatic polymers is disclosed. The process entails using a supported catalyst wherein support contains alumina and where the catalyst comprise least one metal of subgroup VIII of the Periodic Table. The catalyst is characterized in that the pore volume of the pores having diameters of 1000 to 10,000 Angstrom is 15 to 100% relative to the total pore volume, as determined by mercury porosimetry. "

IN THE CLAIMS:

Please amend the claims as follows:

5. A process according to Claim 1 wherein the catalysts have a pore volume, as measured by nitrogen sorption, of less than 10% for pore diameters less than 600 A.

6. A process according to Claim 1 wherein the metals are selected from nickel, platinum, ruthenium, rhodium and palladium.

7. A process according to Claim 1 wherein the process is conducted in the presence of solvents which can be used for hydrogenation reactions.

8. A process according to Claim 1 wherein the catalyst has a specific surface greater than 5 m²/g.

Please add the following:

--9. A process for hydrogenating aromatic polymers comprising using a supported catalyst wherein support contains alumina and where the catalyst comprise at least one metal of subgroup VIII of the Periodic Table, said catalyst characterized in that the pore volume of the pores having diameters of 1000 to 10,000 Angstrom, is 15 to 100% relative to the total pore volume, said pore volume determined by mercury porosimetry. --

REMARKS

The present amendment seeks to place the application in better conformance with U.S. practice. A page containing an Abstract of the disclosure is enclosed.

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is titled "VERSION WITH MARKINGS TO SHOW CHANGES MADE"

Entry of the amendment is requested.

Respectfully submitted,

VOLKER WEGE
KONSTADINOS XOUZINAS
JOHANN RECHNER

By



Aron Preis
Attorney for Applicants
Reg. No. 29,426

Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-8341
FACSIMILE PHONE NUMBER:
(412) 777-8363
s:\kgl\ap2409pa

Mo-6479

Version with markings to show changes made

Delete the Title of the application - appearing in pages 1 and 13 - and insert therefor:

-- Method for Hydrogenating Aromatic Polymers in the Presence of Special Catalysts --.

IN THE ABSTRACT:

Please revise the Abstract of the disclosure at page 13 to read:

"A process for hydrogenating aromatic polymers is disclosed. The process entails using a supported catalyst wherein support contains alumina and where the catalyst comprise least one metal of subgroup VIII of the Periodic Table. The catalyst is characterized in that the pore volume of the pores having diameters of 1000 to 10,000 Angstrom is 15 to 100% relative to the total pore volume, as determined by mercury porosimetry. "

Please amend the claims as follows

5. A process according to [one or more of the preceding claims,] Claim 1 wherein the catalysts have a pore volume, as measured by nitrogen sorption, of less than 10% for pore diameters less than 600 A.

6. A process according to [one or more of the preceding claims,] Claim 1 wherein the metals are selected from nickel, platinum, ruthenium, rhodium and palladium.

7. A process according to [one or more of the preceding claims,] Claim 1 wherein the process is conducted in the presence of solvents which can be used for hydrogenation reactions.

8. A process according to [one or more of the preceding claims,] Claim 1 wherein the catalyst has a specific surface greater than 5 m²/g.

Please add the following:

--9. A process for hydrogenating aromatic polymers comprising using a supported catalyst wherein support contains alumina and where the catalyst comprise at least one metal of subgroup VIII of the Periodic Table, said catalyst characterized in that the pore volume of the pores having diameters of 1000 to 10,000 Angstrom, is 15 to 100% relative to the total pore volume, said pore volume determined by mercury porosimetry. --

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METHOD FOR HYDROGENATING AROMATIC POLYMERS
IN THE PRESENCE OF SPECIAL CATALYSTS

ABSTRACT OF THE DISCLOSURE

A process for hydrogenating aromatic polymers is disclosed. The process entails using a supported catalyst wherein support contains alumina and where the catalyst comprise at least one metal of subgroup VIII of the Periodic Table. The catalyst is characterized in that the pore volume of the pores having diameters of 1000 to 10,000 Angstrom is 15 to 100% relative to the total pore volume, as determined by mercury porosimetry.

A process for the hydrogenation of aromatic polymers in the presence of special catalysts

- The present invention relates to a process for the hydrogenation of aromatic polymers, which is characterised in that metals of subgroup VIII of the periodic table are present, together with a support comprising alumina. The catalysts have a special pore volume distribution. By this means, the aromatic units of aromatic polymers can be hydrogenated completely and without significant reduction of their molecular weights.
- The hydrogenation of aromatic polymers is already known. DE-AS 1 131 885 describes the hydrogenation of polystyrene in the presence of catalysts and solvents. Aliphatic and cycloaliphatic hydrocarbons, ethers, alcohols and aromatic hydrocarbons are mentioned as solvents. A mixture of cyclohexane and tetrahydrofuran is stated to be preferred. Silica and alumina supports for the catalysts are mentioned in general, but the physicochemical structure thereof is not described.

- EP-A-322 731 describes the production of what are predominantly syndiotactic polymers based on vinylcyclohexane, wherein a styrene-based polymer is hydrogenated in the presence of hydrogenation catalysts and solvents. Cycloaliphatic and aromatic hydrocarbons are mentioned as solvents, but ethers are not mentioned.

- DE 196 24835 (= EP-A 814 098), which relates to the hydrogenation of polymers using ruthenium or palladium catalysts in which the active metal is deposited on a porous support, describes the hydrogenation of olefinic double bonds of polymers.

- Aromatic regions are hydrogenated by less than 25 %, and in general are hydrogenated within a range from 0 to about 7 %. The choice of solvent is not critical.

- It is also known (WO 96/34896 = US-A-5,612,422) that silica-supported catalysts for the hydrogenation of aromatic polymers, which catalysts have small pore diameters (200-500 Å) and large specific surfaces (100-500 m²/g), can result in incomplete hydrogenation and to a breakdown of the polymer chain. The use of special silica-

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Donna J. Veatch

(Name of person mailing paper or fee)

supported hydrogenation catalysts (WO 96/34896) enables what is almost complete hydrogenation to be achieved with a reduction of about 20 % in molecular weights. These catalysts comprise a special pore size distribution of the silica, which is characterised in that 98 % of the pore volume corresponds to a pore diameter larger than 600 Å. Said catalysts have specific surfaces between 14-17 m²/g and average pore diameters of 3800-3900 Å. Dilute solutions of polystyrene in cyclohexane, with a concentration ranging from 1% to a maximum of 8 %, are hydrogenated with degrees of hydrogenation greater than 98 % and less than 100 %.

- 10 The examples described in the documents cited above indicate a reduction in the absolute molecular weight of hydrogenated polystyrene at polymer concentrations less than 2 %. In general, a reduction in molecular weight results in a deterioration in the mechanical properties of a hydrogenated polystyrene.
- 15 The comparative example in WO 96/34896, in which a commercially available 5 % Rh/Al₂O₃ catalyst is used (Engelhard Corp., Beachwood, Ohio, USA) results in a degree of hydrogenation of 7 % and indicates the lower activity of an alumina support compared with a silica-supported catalyst.
- 20 Surprisingly, it has now been found that aromatic polymers can be completely hydrogenated without a significant reduction in molecular weight, by using special catalysts, wherein the catalyst is defined in that 10 % at most of its pore volume corresponds to a pore diameter less than 600 Å, and it has an average pore diameter greater than 1000 Å and a specific surface greater than 3 m²/g, and comprises a
- 25 defined pore size distribution.

The present invention relates to a process for the hydrogenation of aromatic polymers in the presence of catalysts, wherein a metal or a mixture of metals of subgroup VIII of the periodic table, together with a support comprising alumina, is used as a catalyst, and the pore volume corresponding to the pore diameter of the catalyst between 1000 and 10,000 Å, as measured by mercury porosimetry, is generally 100 - 15 %, 30

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preferably 90 - 20 %, most preferably 80 - 25 %, particularly 70 to 30 %, with respect to the total pore volume as measured by mercury porosimetry.

5 The average pore diameter, as determined by mercury porosimetry, is greater than 1000 Å.

However, the mercury method is only satisfactory for pores which are larger than 60 Å. Pore diameters smaller than 600 Å are therefore determined by nitrogen sorption as described by Barret, Joyner and Halenda (DIN 66 134).

10 The catalysts have a pore volume as measured by nitrogen sorption of less than 10 %, preferably less than 5 %, for pore diameters less than 600 Å. The pore volume as measured by nitrogen sorption is quoted with respect to the total pore volume as measured by mercury porosimetry.

15 The average pore diameter and the pore size distribution are determined by mercury porosimetry according to DIN 66 133.

20 The average pore diameter generally ranges from 1000 Å to 10,000 Å, preferably from 2000 Å to 7000 Å, most preferably from 2500 Å to 6000 Å.

Methods for the characterisation of hydrogenation catalysts are described in WO 96/34896 (=US-A-5,612,422), and in Applied Heterogeneous Catalysis, Institute Français du Pétrole Publication, pages 189-237 (1987), for example.

25 The catalysts consist of metals of subgroup VIII, which are present together with a support comprising alumina.

30 Aluminas of general chemical formula Al_2O_3 occur in various modifications. A distinction is made, for example, between hexagonal $\alpha\text{-Al}_2\text{O}_3$ and face-centred cubic crystalline $\gamma\text{-Al}_2\text{O}_3$. $\beta\text{-Al}_2\text{O}_3$ is understood to comprise a group of aluminas which contain small amounts of extraneous ions in their crystalline lattice. Other special

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modifications exist, and numerous transitional forms exist between aluminium hydroxides and aluminas.

The specific surface of the catalyst is determined by the BET (Brunauer, Emmett and
5 Teller) method using nitrogen adsorption according to DIN 66 131 and DIN 66 132.

The (BET) specific surfaces for nitrogen are generally greater than 3 m²/g, and preferably range from 5 m²/g to 80 m²/g, most preferably from 8 m²/g to 60 m²/g.

10 Metals of subgroup VIII are generally used, preferably nickel, platinum, ruthenium, rhodium, or palladium, most preferably platinum or palladium.

The metal content is generally 0.01 to 80 %, preferably 0.05 to 70 % with respect to the total weight of catalyst.

15

In a process which is operated as a batch process, the 50 % value of the cumulative distribution of particle size generally ranges from 0.1 µm to 200 µm, preferably from 1 µm to 100 µm, most preferably from 3 µm to 80 µm.

20 The usual solvents for hydrogenation reactions are aliphatic or cycloaliphatic hydrocarbons, aliphatic or cycloaliphatic saturated ethers, or mixtures thereof, e.g. cyclohexane, methylcyclopentane, methylcyclohexane, ethylcyclohexane, cyclooctane, cycloheptane, dodecane, dioxane, diethylene glycol dimethyl ether, tetrahydrofuran, isopentane and decahydronaphthalene.

25

If aliphatic or cycloaliphatic hydrocarbons are used as solvents, they preferably contain water in a amount which ranges in general from 0.1 ppm to 500 ppm, preferably from 0.5 ppm to 200 ppm, most preferably from 1 ppm to 150 ppm, with respect to the total solvent.

30

The process according to the invention generally results in what is practically the complete hydrogenation of the aromatic units. As a rule, the degree of hydrogenation

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is $\geq 80\%$, preferably $\geq 90\%$, most preferably $\geq 99\%$ to 100% . The degree of hydrogenation can be determined by NMR spectrometry or UV spectroscopy, for example. The process according to the invention most preferably results in hydrogenated aromatic polymers, particularly polyvinylcyclohexane, wherein the amount of dyads with a syndiotactic configuration is greater than 50.1% and less than 74% , particularly 52 to 70% .

Aromatic polymers are used as the starting materials, and are selected, for example, from polystyrenes which are optionally substituted on their phenyl ring or on their vinyl group, or from copolymers thereof with monomers selected from the group comprising olefines, (meth)acrylates or mixtures thereof. Other suitable polymers include aromatic polyethers, particularly polyphenylene oxide, aromatic polycarbonates, aromatic polyesters, aromatic polyamides, polyphenylenes, polyxylylenes, polyphenylene vinylenes, polyphenylene ethinylenes, polyphenylene sulphides, polyaryl ether ketones, aromatic polysulphones, aromatic polyether sulphones, aromatic polyimides and mixtures thereof, and optionally copolymers with aliphatic compounds also.

Suitable substituents in the phenyl ring include C_1 - C_4 alkyl groups, such as methyl or ethyl, C_1 - C_4 alkoxy groups such as methoxy or ethoxy, and aromatic entities which are condensed thereon and which are bonded to the phenyl ring via a carbon atom or via two carbon atoms, comprising phenyl, biphenyl and naphthyl.

Suitable substituents on the vinyl group include C_1 - C_4 alkyl groups such as methyl, ethyl, or n- or iso-propyl, particularly methyl in the α -position.

Suitable olefinic comonomers include ethylene, propylene, isoprene, isobutylene, butadiene, cyclohexadiene, cyclohexene, cyclopentadiene, norbornenes which are optionally substituted, dicyclopentadienes which are optionally substituted, tetracyclododecenes which are optionally substituted, and dihydrocyclopentadienes which are substituted,

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C₁-C₈, preferably C₁-C₄ alkyl esters of (meth)acrylic acid, preferably methyl and ethyl esters,

5 C₁-C₈, preferably C₁-C₄ alkyl ethers of vinyl alcohol, preferably methyl and ethyl ethers,

C₁-C₈, preferably C₁-C₄ alkyl esters of vinyl alcohol, preferably vinyl acetate,

10 derivatives of maleic acid, preferably maleic anhydride, derivatives of acrylonitrile, preferably acrylonitrile and methacrylonitrile.

The preferred polymers are polystyrene, polymethylstyrene, and copolymers of styrene and at least one other monomer selected from the group consisting of α -methylstyrene, butadiene, isoprene, acrylonitrile, methyl acrylate, methyl
15 methacrylate, maleic anhydride and olefines such as ethylene and propylene for example. Examples of suitable copolymers include those formed from acrylonitrile, butadiene and styrene, copolymers of acrylic esters, styrene and acrylonitrile, copolymers of styrene and α -methylstyrene, and copolymers of propylene, diene and styrene.

20

The aromatic polymers generally have (weight average) molecular weights Mw from 1000 to 10,000,000, preferably from 60,000 to 1,000,000, most preferably from 70,000 to 600,000, particularly from 100,000 to 480,000, as determined by light scattering.

25

The polymers can have a linear chain structure or can have branching locations due to co-units (e.g. graft copolymers). The branching centres may comprise star-shaped or branched polymers, or may comprise other geometric forms of the primary, secondary, tertiary or optionally of the quaternary polymer structure.

30

The copolymers may exist as random copolymers or alternatively may exist as block copolymers.

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Block copolymers comprise di-blocks, tri-blocks, multi-blocks and star-shaped block copolymers.

- 5 The initial polymers which are used are generally known (e.g. WO 94/21694).

The amount of catalyst to be used is described in WO 96/34896, for example.

- 10 The amount of catalyst used depends on the process which is carried out. This process can be conducted continuously, semi-continuously or batch-wise.

- 15 In a continuous system, the time of reaction is considerably shorter: it is influenced by the dimensions of the reaction vessel. In a continuous procedure, it is possible to use a trickling system or a liquid pool system, which both employ fixed catalysts, and it is also possible to use a system comprising a suspended catalyst, which can be recycled for example. Fixed catalysts can exist in the form of tablets or as an extruded product, for example.

- 20 The polymer concentrations with respect to the total weight of solvent and polymer generally range from 80 to 1, preferably from 50 to 10, particularly from 40 to 15 % by weight.

- 25 The reaction is generally conducted at temperatures between 0 and 500°C, preferably between 20 and 250°C, particularly between 60 and 200°C.

- The reaction is generally conducted at pressures from 1 bar to 1000 bar, preferably from 20 to 300 bar, particularly from 40 to 200 bar.

- 30 The palladium catalyst can be used either in reduced form or in unreduced form in the reaction concerned, whilst maintaining a comparable activity. In an industrial process, it is considerably more advantageous to employ the catalyst in unreduced form and not to have to carry out an additional, costly catalyst reduction step as in WO 96/34 896.

Examples:

5 The absolute (weight average) molecular weights M_w of the initial polymer and of the hydrogenated product were determined by light scattering. The absolute (number average) molecular weights M_n were determined by membrane osmosis. In Example 2, the relative M_w value obtained from the GPC determination (gel permeation chromatography using tetrahydrofuran as the elutant) compared with a polystyrene standard corresponded to the absolute molecular weights which were determined for
10 the polystyrene used.

Examples 1 and 2

15 The catalysts used in the examples are characterised in Table 1.

A 1 litre autoclave was flushed with inert gas. The polymer solution and optionally the unreduced catalyst were added (Table 2). After closing the autoclave, it was repeatedly pressurised with a protective gas and then with hydrogen. After releasing the pressure, the respective hydrogen pressure was set and the batch was heated with
20 stirring to the corresponding reaction temperature. After the consumption of hydrogen had commenced, the reaction pressure was held constant.

The time of reaction was the time from heating up the batch until complete hydrogenation was effected of the polystyrene, or was the time until the consumption
25 of hydrogen tended towards its saturation value.

After the reaction was complete, the polymer solution was filtered. The product was precipitated in methanol and dried. The isolated product had the physical properties listed in the Table.

Table 1: Physical characterisation of the catalysts used

Catalyst No.	Nitrogen pore volume for pore diameters of < 600 Å mm ³ /g	Total mercury pore volume for pore diameters from 38 Å - 15 µm mm ³ /g	Mercury pore volume for pore diameters from 1000 Å - 10,000 Å mm ³ /g	N ₂ pore volume for pore diameters of < 600 Å / total mercury pore volume %	Pore volume for pore diameters of 1000 Å - 10,000 Å / total mercury pore volume (38 Å - 15 µm) %	Average pore diameter ¹ Å	Total specific surface (BET) ² m ² /g	Metal content %
I	32	767	480	4	63	2722	11.9	0.5

Catalyst: Engelhard De Meern, Holland, C 586-102, palladium on alumina

- 1) average pore diameter as measured by mercury porosimetry
- 2) total specific nitrogen surface according to Brunauer, Emmett and Teller (BET, DIN 66131, DIN 66132)

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Table 2:

Hydrogenation of polystyrene as a function of the catalyst, solvent system and reaction temperature

Example No.	Catalyst	Weight of polymer g	Solvent ³⁾ ml	Weight of catalyst g	Reaction temperature °C	H ₂ pressure bar	Time of reaction min	Degree of hydrogenation ⁴⁾ %	T _g (DSC) °C	M _w 10 ³ g/mol
1 (comparative) US-A 5612422	5 % Pt/SiO ₂	200 ¹⁾ M _w ~ 200,000 g mol ⁻¹	2300 CH	13.5	150	875 (psig)	110	98.4	146.6	-
2 according to the invention	0.5 % Pd/Al ₂ O ₃ ⁵⁾	100.2 ²⁾	300 CYH	12.5	200	100	130	100	147	171

¹⁾ polystyrene (M_w ~ 200,000 g mol⁻¹)²⁾ polystyrene type 158 k; M_w = 280,000 g/mol, BASF AG, Ludwigshafen, Germany³⁾ CYH = cyclohexane⁴⁾ determined by ¹H NMR spectrometry⁵⁾ Engelhard De Meern, Holland, palladium on alumina, C586-102

5 The platinum catalyst according to Example 5 of US-A 5 612 422 resulted in a decrease of about 20 % in the molecular weight Mw.

A decrease in molecular weight results in particular in a reduction of the average molecular weight Mw (US-A 5 612 422). Surprisingly, hydrogenation according to the invention in the presence of the alumina catalyst resulted in no significant decrease in the absolute molecular weight Mw, even at elevated temperatures of reaction.

Within the range of accuracy of the measurements, the absolute average molecular weight M_w of the hydrogenated product corresponded to that of the polystyrene used.

15 Compared with comparative example 1, the special alumina catalyst of the present invention resulted in a comparable time of reaction, but with complete hydrogenation being achieved at the same time, using a polystyrene of higher molecular weight and at a higher polymer concentration.

20

The catalyst is distinguished by a weight of noble metal which is less by a factor of 10, which results in a significant reduction in raw material costs and which thus improves the economics of the hydrogenation process.

A process for the hydrogenation of aromatic polymers in the presence of special catalysts

Abstract

A process for the hydrogenation of aromatic polymers in the presence of catalysts, wherein a metal or a mixture of metals of subgroup VIII of the periodic table, together with a support comprising alumina, is used as a catalyst, and the pore volume corresponding to the pore diameter of the catalyst between 1000 and 10,000 Å, as measured by mercury porosimetry, is generally 100 - 15 % with respect to the total pore volume as measured by mercury porosimetry.

COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR HYDROGENATING AROMATIC POLYMERS IN THE PRESENCE OF SPECIAL CATALYSTS

the specification of which is attached hereto,

or was filed on **January 26, 2000**

as a PCT Application Serial No. **PCT/EP00/00576**



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I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 04 612.3
(Number)

Germany
(Country)

February 5, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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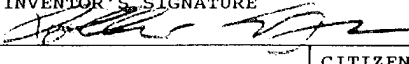

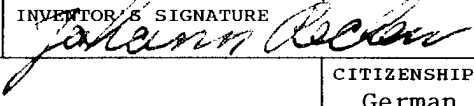
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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office conne

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426
 LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY,
 Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619
 GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office
 Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138
 DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office
 Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552
 JACKIE ANN ZURCHER, Patent Office Registration Number 42,251
 RAYMOND J. HARMUTH, Patent Office Registration Number 33,896

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: Direct Telephone Calls To:
 Patent Department
 Bayer Corporation (412) 777-2349
 100 Bayer Road
 Pittsburgh, Pennsylvania 15205-9741

FULL NAME OF SOLE OR FIRST INVENTOR <u>Volker Wege</u>		INVENTOR'S SIGNATURE 	DATE <u>05-07-00</u>
RESIDENCE D 41470 <u>Neuss</u> , Germany		CITIZENSHIP German <u>DEX</u>	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF SECOND INVENTOR <u>Konstadinos Douzinas</u>		INVENTOR'S SIGNATURE 	DATE <u>2001-07-09</u>
RESIDENCE D 51061 <u>Köln</u> , Germany		CITIZENSHIP Greek <u>DEX</u>	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF THIRD INVENTOR <u>Johann Rechner</u>		INVENTOR'S SIGNATURE 	DATE <u>2001-08-06</u>
RESIDENCE D 47906 <u>Kempen</u> , Germany		CITIZENSHIP German <u>DEX</u>	
POST OFFICE ADDRESS Friedrich-Kramer-Str. 2, D 47906 Kempen, Germany			
FULL NAME OF FOURTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			